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Title: Pulsed light for a cleaner dyeing industry: azo dye degradation by an advanced oxidation process driven by pulsed light

Article Type: Original article

Keywords: Pulsed light; advanced oxidation process; azo dye; wastewater remediation; ferrioxalate

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Abstract: Water pollution by wastewater containing dyes is an environmental issue that can be mitigated by the use of advanced oxidation processes (AOP). Pulsed light (PL) is an emerging food processing technology that uses eco-friendly lamps and can potentially be adapted as light source of an UV-based AOP. In the present work, a PL/H₂O₂ process was tested for the decolourization of two azo dyes, and a pulsed light/H₂O₂/ferrioxalate process was tested for the decolourization of one azo dye. The efficiency of the PL/H₂O₂ process in a batch reactor under different parametric values: dye concentration, pH, H₂O₂ and salt doses was followed by spectrophotometry and fitted to first-order kinetics; and several degradation products were detected. In the PL/H₂O₂ process, decolourization rates increased at low dye concentrations and high H₂O₂ doses, were pH-dependent and were inhibited by the addition of NaCl, Na₂SO₃ or Na₂CO₃. More than 50 % decolouration was achieved with the PL/H₂O₂ process for both dyes after applying 54 J/cm² (25 light pulses). The PL/H₂O₂/ferrioxalate process achieved > 95 % decolouration for Methyl orange when applying 21 J/cm² (10 pulses); that level of energy can be supplied by PL commercial systems in nine and four seconds respectively. No known toxic degradation products were detected. Results show that a PL/H₂O₂ process has potential to be used for the efficient degradation of dyes from wastewater. Furthermore, the efficacy of this process can be improved by the use of ferrioxalate. PL technology could become an alternative light source to contribute to decrease the environmental impact of wastewater produced by the dyeing industry.

We are very thankful for all the suggestions. We have never had so many suggestions for improving a manuscript, and it has taken much time to fulfill all the requests, including new determinations. However, we consider that the requests have been very useful for improving our manuscript.

Besides attending all remarks, we inform that we have introduced two additional changes.

The first one is that we have deleted all information related to Direct red 83:1 dye. This decision was taken because we were unable to detect intermediaries of the degradation of this dye in spite of we sub-contracted a top analytical laboratory. Therefore, we believe that we should not report the full data from three dyes (Congo red, Direct red 83:1 and Methyl orange) but reporting intermediaries for only two. This decision also took into consideration that the validity of the study and its conclusions also remain valid in spite of excluding the third day from our manuscript. Furthermore, if data on Direct red 83:1 would have left, it would have made the manuscript excessively long, since new data and discussion was added after reviewer's comments.

The second change is that we have included a new co-author. She is the leader of the laboratory that was sub-contracted for the study of degradation products. We believe that her effort and input has gone beyond what we have paid, and that she has made a significant contribution to our study from the scientific point of view.

Reviewers' comments:

Editor: Please make sure to clearly demonstrate the relevance of your study to sustainability and cleaner production in the introduction.

Some pertinent comments have been added to the text.

Reviewer #1: Reviewer comments for JCLEPRO-D-18-00919

General comment: In this manuscript, the authors used a PL/H₂O₂ process and a PL/H₂O₂/ferrioxalate process to test the decolourization of azo dye. Generally the analytical method applied was proper, and the datasets seemed reliable. The manuscript is acceptable for publication after being major revised. And I have below revision suggestions and comments for the authors to consider:

1. **Key word "dye" should be changed to "azo dye".**

Changed accordingly.

2. **Figure's format should be consistent. In Fig 1, the pattern B is different from A and C?**

Figures were redrawn to the same format.

3. **Does the pulse interval have any effect on dye degradation? What is the effect of sustained light degradation?**

Answers to this query have been provided in the modified manuscript in introduction and discussion sections.

4. **There are too many grammatical mistakes in this manuscript, which causes great obstacle to reading. Thus polishing is suggested.**

The new version of the manuscript has been revised by a native speaker.

For example, Page 2 Line 5-6 "has in advanced oxidation processes (AOP) a set of technologies used to mitigate it." is a wrong expression. It should be revised as "a set of advanced oxidation processes (AOP) technologies used to mitigate it".

The sentence has been reworded.

Line 33-38: "as an alternative for efficient water treatment (technology) " and "before (they) to be released to the environment", this sentence is so long that its subjects are rather confusing. This sentence should be divided into three sentences or more.

The sentence has been reworded and divided.

5. **Page 2 Line 22-23: "decreased by NaCl, Na₂SO₃ and Na₂CO₃". What are decreased, their dose or other? It wasn't expressed clearly.**

The sentence was rephrased in order to improve clarity.

6. **Page 5 line 37-38 "Fe++" should be written as "Fe²⁺". Line 1, Page 31: "38.8 mg/L Fe +3 , 8.7 mg/L C₂O₄ -2" were in a wrong expression.**

The text has been modified accordingly. Additionally, English was polished throughout the text.

7. **Page 11, Line 35. This viewpoint should be supported by the relevant literatures.**

The viewpoint has been supported by the absorption spectra reported in this manuscript and by relevant literature.

8. The lines of the graphics need to be corrected. For example, the lines of the figures in Page 15 were not clear

The lines have been thinned for better differentiation.

, and the lines of the figures in Page 19 were presented in different sizes.

Figures have been harmonized for the modified manuscript in terms of line size, colors, line type and symbols.

9. Experimental description is confusing. For example, Page 2 Line 38-42: "The integration of PL technology as a light source in an AOP can provide very fast dye degradation, which would allow cleaner dyeing industries." this sentence was wrong, the writer should pay attention to it.

The sentence has been replaced by a new one in the modified manuscript.

Page 11 Line 33-34, " were " should be " was ".

Corrected.

Page 32 line 40: "by decreasing the environmental pollution caused by their effluents." This sentence should be modified.

The sentence has been replaced by a new one in the modified manuscript.

10. There are no data supporting that PL/ H₂O₂ process was better than UV/ H₂O₂.

The original manuscript supplies some comparisons between the PL/H₂O₂ process and other processes (sections 3.1 and 3.8) together with a warning on the inaccurate character of such kind of comparisons. In both cases, the time needed to attain certain level of dye degradation is referred. We believe that given the difference of experimental set ups between our and others works (reactor configuration, type of dye, dye concentration, volume of treated solution, residence time if continuous, solution flow if continuous, etc.), extending the discussion can lead to misleading conclusions by some readers.

New experimental data showing performance of an UV/ H₂O₂ process could have been produced by us and added to the manuscript. However, we strongly believe that comparisons on the efficacy of light sources can only be accurately found by using reactors of identical characteristics and following strict protocols. Collimated reactors would be ideal for this aim. Even though there are collimated CW UV reactors, equivalent pulsed light reactors do not exist. We have recently proposed such kind of systems for pulsed light technology (Gómez-López and Bolton, 2016), but they do not exist yet. That is why, even though we have a CW UV

light system in our laboratory, we refrain ourselves from comparing data between both of our light systems.

Gómez-López, V.M.; Bolton, J.R. 2016. An approach to standardize methods for fluence determination in bench-scale pulsed light experiments. *Food and Bioprocess Technology*, 9, 1040-1048. DOI 10.1007/s11947-016-1696-z.

Furthermore, we believe that evaluating the electrical energy consumption of the system may be an interesting alternative for comparing PL with other light generation technologies. We supply below tables with respective calculations for Congo red and Methyl orange degraded under our standard conditions. We would also like to comment how we adapted the equation to the specific case of pulsed light technology. Yet, we then justify why we did not include this in the last version of the manuscript.

We have used for this evaluation equation 8a of the classical paper of our former co-author Jim Bolton: Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems, *Pure Appl. Chem.*, Vol. 73, No. 4, pp. 627–637, 2001.

We chose equation 8a because it is right one for batch systems. The equation is as this:

$$E_{EO} = \frac{Pt1000}{Vlg(c_i / c_f)}$$

For the specific case of pulsed light, the electrical consumption of the system is not constant. Pulsed light technology is based in power compression technologies, where the electrical energy is stored in capacitors, and then released to the lamp to produce light. This means that the process happens in two phases, in the first one the capacitors are charged. In the second one, the energy stored in the capacitors is released to the lamp and the treatment of the sample actually occurs. Therefore, we measured (long time ago, before starting the tests for the current manuscript) the amperage during the duty cycle and realize that, as expected, the electrical consumption only occurs during the time capacitors are charged and it is null when not. We also measured the time that takes to charge capacitors to the desired voltage (2,500 V), and it was four seconds. Therefore, the treatment time we chose for our calculations was the charging time (4 seconds) of the capacitors multiplied by the number of pulses (45 pulses). The calculations can be observed in the following tables.

Congo red		
Parameter	Value	Unit
V	0.220	kV
A	1.43	A
P	0.31	kW
Charging time	4	s
# pulses	45	Pulses
Total charging time	180	s
Total charging time	0.05	h
kW h	0.016	kW h
Sample volume	0.020	L
Sample volume	0.00002	m ³
C _i	0.527	mg/L
C _f	0.064	mg/L
log (C _i /C _f)	0.92	
E_{EO}	856	kW h/m ³ /order

Methyl orange		
Parameter	Value	Unit
V	0.220	kV
A	1.43	A
P	0.31	kW
Charging time	4	s
# pulses	45	Pulses
Total charging time	180	s
Total charging time	0.05	h
kW h	0.016	kW h
Sample volume	0.020	L
Sample volume	0.00002	m ³
C _i	0.740	mg/L
C _f	0.013	mg/L
log (C _i /C _f)	1.77	
E_{EO}	444	kW h/m ³ /order

Why did not report these if we can calculate it?

The point is that we have used a non-submerged bench top device. Therefore, only part of the light emitted by the lamp actually impinges the sample surface. How big is the fraction of light that really carries out the treatment? It cannot be estimated, but observing the reactor leads us to think that most part of the light is lost. Therefore, reporting our calculation would yield to a serious overestimation of the electrical energy per order of our experiments.

Additionally, the last article by Jim Bolton on the subject: Standard reporting of Electrical Energy per Order (EEO) for UV/H₂O₂ reactors (IUPAC Technical Report)

<https://doi.org/10.1515/pac-2017-0603>, in section 3.6 “Common mistakes when applying the EEO parameter” warns about the use of this parameter on the kind of systems that we have used.

11. Did you quantify the hydroxyl radicals that come from the reaction driven by pulsed light?

According to your suggestion, the role of hydroxyl radicals in dye degradation was tested by using ethanol as hydroxyl scavenger. Before it, the use of t-butanol, which is more commonly used as hydroxyl scavenger than ethanol, was tested. However, its use was ruled out from our experiments because it changed the colour of Congo red solution immediately.

12. Page 20-22: in these tables, the blank bars should be added.

Blanks were added accordingly.

13. Page 30, line 30: About the effect of ferrioxalate complex on Methyl orange decolourization, there are no data or graph to support the results.

In page 30, line 30, the effect of ferrioxalate complex is stated as a hypothesis. The verification of the validity of this hypothesis is given in the next paragraph based on data from table 4, where the data requested by the reviewer is given in the original manuscript.

Yet, the fact that the reviewer did not realize that the information was in the manuscript lead us to the conclusion that it was not clear enough in this regard. Therefore, we have included an additional statement in the modified manuscript.

14. Page 32 line11: please change "Fast colourization of three..." as "Fast decolourization of three ..."

Changed accordingly.

15. There are no error bars in the figures, please revise

Error bars have been included in the figures. Sometimes are very small and get hidden by point symbols.

16. Page 33, line 50 and Page 35, line 54: Some references are too old;

We understand the reviewer's concern but we also believe that the references are pertinent. Those references are from basic research, where kinetic constants and other basic information have been reported, and have been widely cited in the literature. We have made efforts to trace the source of every piece of information used in our literature review back to its original authors, which has included the task of finding the original articles published many years ago.

Alternatively, we could have cited new articles where those old articles have been cited; which would make our manuscript looks updated but it would violate the rule (not followed by everybody) of citing primary references. Additionally, other old articles such as those by Galindo, are pioneer works highly cited by other authors. Finally, new articles deal mainly with the synthesis of photocatalyzers, while the UV/H₂O₂ system or even the ferrioxalate method are old and as consequence the references related to them. We have justified in the original manuscript why we chose to work with such simple degradation methods.

Page 36, line 50: This reference is in a different format.

The reference was reformatted.

Title: Pulsed light for a cleaner dyeing industry: azo dye degradation by an advanced oxidation process driven by pulsed light

The present study describes the use of physico-chemical method: pulsed light in association with H₂O₂ (Advanced Oxidation Process) for treatment for azo dyes. The study is timely, since azo dyes are one of the prominent pollutants across the globe. Authors have disillusioned in the entire study, by major experimental lacuna noted below. It would be difficult to accept the current manuscript, because the study requires further experimentation to support the obtained preliminary results.

1. Page # 9: Section 2.3: One of the major shortcomings at experimental stage is mere 20 ml of the dye solution was used. Even at laboratory scale 20 ml reaction system makes no sense. I did not get any strong and logical perspective with this experiment. Can it be scientifically, technically, statistically and environmentally relevant?

We understand the reviewer's concern when we compare our work with others with similar goals. However, it should also be understood that pulsed light technology is a relatively new method with scarce availability of different models of hardware. For example, there is not currently in the market pulsed light systems for liquid treatment.

While the construction of their own reactors by researchers of the UV light research field is relatively common, this is not an option in pulsed light technology, which requires sophisticated electronic circuits to manage electric tensions in the order of kilovolts. Pulsed light systems come from factory with lamps fixed to fits and surrounded by wires, which does not allow to take the lamp out of the carcass. Please, see a picture of our pulsed light system without carcass below.

These pulsed light systems have been designed mainly for inactivation of microorganisms in Petri dishes, therefore, experiments using this technology are limited by small treatment chambers. As any other “starting” research field, we had to choose between waiting who knows how long (maybe years) to have the proper device or working with the hardware currently available; we obviously chose the latter option.

You can see our pulsed light system (manufactured by Steribeam) in the picture below, the lamp is at the top of the treatment chamber and cannot be viewed in the picture. You can realize that the space is scarce.

Other options are the Claranor system (<http://www.claranor.com/>). It is a very big system but at the end of the day, the space in the chamber is also limited. You can see a picture below. A Petri dish is visible in it and the lamps (three in this case) are in the part exactly above the Petri dish.

The third big manufacturer of this kind of equipment is Xenon corp. (<http://www.xenoncorp.com/>), and a picture of its device can be seen below. The limitation for treating high volume of liquids of all these systems is obvious.

If you have previous awareness of this technology, or make a search about it, you may still find some flow-through or falling-film devices in the literature, but they are not manufactured anymore and the researchers that own them are not active anymore in the area.

You can find a Xenon Corp. flow-through reactor used in: Disinfection of synthetic and real municipal wastewater effluent by flow-through pulsed UV-light treatment system, <https://doi.org/10.1016/j.jwpe.2016.02.004>. You can confirm that they are not manufactured anymore at these contact mails: P.Schullerer@polytec.de (if you are in Europe) or info@xenoncorp.com for USA or the rest of the world.

You can also find a Claranor flow-through reactor in: Decontamination of Sugar Syrup by Pulsed Light, doi:10.4315/0362-028X.JFP-11-342. Or a Claranor falling-film reactor in: Factors affecting microbial inactivation by Pulsed Light in a continuous flow-through unit for liquid products treatment, doi:10.1016/j.profoo.2011.09.119. You can mail to amoutier@claranor.com, if you want to confirm that they are not available anymore.

The other pulsed light system manufacturer, Steribeam, has no known flow-through system, you can reach it at: info@steribeam.com.

In conclusion, we worked with state-of-the-art equipment and we did not have many options for our experiments. Either we worked with the limitations that the pulsed light systems available on the market have or we did not test this technology at all.

2. Page # 9: Section 2.3: What constitute a 1 pulse? Describe completely.

The characteristics of the pulse were fully described in the original manuscript. Since this query led us think that the text was not clear enough even though the information was there, the paragraph was rearranged to improve clarity. The description of the light pulse appears now in a separated paragraph. Additionally, some words in the rest of the text were inserted in order to make clear that when the word “pulse” is written, it means “light pulse”.

3. Page # 9: Section 2.3: Line # 32-33: Show the results in graphical form (overlapping of the entire spectra to demonstrate the non-existence of isosbestic point), at least in supplementary section.

One figure (Fig. S1) has been included as supplementary material.

4. Page # 10: Section 2.3: Line # 12: Inhibitors (NaCl, Na₂SO₃ or Na₂CO₃). Do they inhibit during pulse or entire treatment procedure?

It was not the aim of the work reported in this manuscript to go in deep on every aspect of this novel method. However, since the manuscript seems to require more explanation, a brief comment has been included in the modified manuscript.

5. Page # 11: Section 3.1: Line # 35-36: "... (data not shown).", should be avoided. Especially when the entire experimental system is of only 20 ml, how had authors anticipated not to show the data?

Data is shown in the modified manuscript.

6. It is well established fact that, decolourization of azo dyes, does not reduce the toxic nature of the compound. Have authors studied the degradation behaviour of dyes used in the study?

Results on the degradation behavior of dyes used in the study have been incorporated.

7. It is another well established fact that, physico-chemical methods during dye treatment produce by-products which often toxic and requires secondary treatment. Since H₂O₂ and ferrioxalate were used, which would react to dye compounds and might have produced secondary compounds (and was not characterized in this study), what could be the relevant outcome of experiments performed?

The characterization of secondary has been carried out for the new version of the manuscript.

Pulsed light for a cleaner dyeing industry: azo dye degradation by an advanced oxidation process driven by pulsed light

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Declaration of interest: none.

Word count: 7452

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Abstract

Water pollution by wastewater containing dyes is an environmental issue that can be mitigated by the use of advanced oxidation processes (AOP). Pulsed light (PL) is an emerging food processing technology that uses eco-friendly lamps and can potentially be adapted as light source of an UV-based AOP. In the present work, a PL/H₂O₂ process was tested for the decolourization of two azo dyes, and a pulsed light/H₂O₂/ferrioxalate process was tested for the decolourization of one azo dye. The efficiency of the PL/H₂O₂ process in a batch reactor under different parametric values: dye concentration, pH, H₂O₂ and salt doses was followed by spectrophotometry and fitted to first-order kinetics; and several degradation products were detected. In the PL/H₂O₂ process, decolourization rates increased at low dye concentrations and high H₂O₂ doses, were pH-dependent and were inhibited by the addition of NaCl, Na₂SO₃ or Na₂CO₃. More than 50 % decolouration was achieved with the PL/H₂O₂ process for both dyes after applying 54 J/cm² (25 light pulses). The PL/H₂O₂/ferrioxalate process achieved > 95 % decolouration for Methyl orange when applying 21 J/cm² (10 pulses); that level of energy can be supplied by PL commercial systems in nine and four seconds respectively. No known toxic degradation products were detected. Results show that a PL/H₂O₂ process has potential to be used for the efficient degradation of dyes from wastewater. Furthermore, the efficacy of this process can be improved by the use of ferrioxalate. PL technology could become an alternative light source to contribute to decrease the environmental impact of wastewater produced by the dyeing industry.

Keywords: pulsed light; advanced oxidation process; azo dye; wastewater remediation; ferrioxalate.

1. Introduction

The disposal of effluent dyes from the textile industry in the environment is an ecological concern due to their toxicity and low degradability. Moreover, dyes are also used for other applications beyond coloration such as in high-technology (optical data storage, light-emitting diodes, etc.), medicine and biomedicine (Singh and Arora, 2011). Arora (2014) estimates that 100,000 tons of dyes are discharged directly in aqueous effluent. It is widely agreed that the disposal of dyes to the environment is a very important problem and that there is an urgent need to develop efficient treatments that decrease water pollution (May-Lozano et al., 2017).

The common biological processes of degradation and discoloration on modern dyes are ineffective because of the high degree of aromatic groups in dye molecules. The traditional physical methods such as using active carbon, filtration, reverse osmosis and coagulation are costly; moreover, these methods do not degrade the dye and just change its phase (Janus and Morawski, 2007; Kaur and Singh, 2007).

Advanced oxidation process (AOP) is a group of technologies that uses hydroxyl radicals for oxidation of target molecules; it has deserved attention in the last years as a mean to degrade dyes. Among the different types of AOPs, the simplest is the generation of hydroxyl radicals from hydrogen peroxide using UV light. The use of novel irradiation sources has been identified as one of the

possible ways to improve the efficacy of AOPs (Lachheb et al., 2002). For example, Congo red has been used to test the efficacy of new light sources such as XeBr, KrCl and Cl₂ excilamps emitting maximum UV radiation at 283, 222 and 259 nm, respectively (Murcia et al., 2011) and an indium gallium nitride light emitting diode (LED) radiating in the range 390-410 nm (Natarajan et al., 2011). Pulsed light (PL) is a photonic technology mainly studied for microbial inactivation, especially in the food technology field, but it is not restricted to it. It consists in the application of pulses of high-intensity broad-spectrum light that includes UV light (Gómez-López et al., 2007). The main feature of PL technology is the production of high photon fluxes. The intermittence of the light emission has not any advantage as such, it is just a consequence of the way the photon flux is generated, which uses a pulsed power energization technique (PPET). A PL system takes energy from the electric main during a relatively long time (milliseconds/seconds), stores it in condensers and then releases it in a short time (microseconds) to one or several lamps. While conventional systems can work at powers of the order of 100-1000 W, PPET can deliver powers of the order of MW, without requiring excessive energy consumption. For example, a PPET system developed 20 years ago was already able to provide 3 MW of electric energy to a lamp while consuming only 3 W from the electric main (MacGregor et al., 1998). Part of the lamp emission is constituted by UV light in different proportions depending on the system manufacturer and operating conditions, these short wavelengths provide high energy photons required by AOPs based on UV light.

One of the characteristics of PL technology is the short treatment time required to attain effects because of the massive generation of photons. Short treatment

times can offer an advantage for the degradation of dyes in textile effluents in terms of speeding up treatments or treating large volumes of wastewater in compact reactors. Additionally, the technology uses eco-friendly lamps filled with Xenon, therefore, it is mercury free, in opposition to the widely used low pressure and medium pressure mercury lamps.

Therefore, PL used as a new light generating technology looks worth investigating due to the possibility of working at high photon fluxes using eco-friendly lamps with modest energy requirements; which may become an interesting alternative for integration in AOPs for the textile industry aimed to reduce the environmental impact caused by its effluents

The incorporation of ferrioxalate complex to an UV/H₂O₂ system enhances dye degradation (Arslan et al., 2000; Monteagudo et al., 2008; Doumic et al., 2015). When ferrioxalate is irradiated in the presence of H₂O₂, Fe²⁺ is produced, which generates hydroxyl radicals (Hislop and Bolton, 1999). An UV-vis/ferrioxalate/H₂O₂ system is more efficient than an UV/H₂O₂ system because of a higher quantum yield and wider absorption spectrum (Safarzadeh-Amiri et al., 1997). The ferrioxalate complex has a much higher molar absorption coefficient than H₂O₂ and absorbs light up to 500 nm (Safarzadeh-Amiri et al., 1997), while PL has a significant emission in the 200-500 nm range (Cudemos et al., 2013); therefore, coupling the ferriolaxate complex to a PL/H₂O₂ AOP may lead to enhanced dye degradation.

Consequently, a series of experiments were designed in order to assess the effectiveness of this new photonic technology as UV light source of an AOP on decolourization of two model azo dyes. The decolourization of Congo red and

Methyl orange solutions was assayed by studying the effect of relevant factors: dye concentration, H_2O_2 concentration, pH and potential inhibitors. Furthermore, the possibility that the ferrioxalate complex accelerates even more dye degradation was tested on Methyl orange.

2. Materials and methods

2.1. Reagents.

Congo red (C. I. 22120; MW: 696.67 g/mol) CAS n° 573-58-0 (fig. 1A) was purchased from Prolabo (Fontenay-sous-Bois, France) and Methyl orange (C. I. 13025; Acid orange 52; MW: 327.33 g/mol), CAS n° 547-58-0 (fig. 1B) was purchased from Sigma-Aldrich (St. Louis, USA). Dyes were used as received. NaCl and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were acquired from Scharlab (Barcelona, Spain), $\text{Na}_2\text{C}_2\text{O}_4$ from VWR (Fontenay-sous-Bois, France) and Na_2CO_3 from Sigma-Aldrich. Ethanol was purchased from Panreac (Barcelona, Spain). Other chemicals were purchased from Merck (Darmstadt, Germany). Solutions were prepared by dissolving the required quantity in milli-Q water >0.2 MΩ. For identification of transformation products (TPs), LC-MS grade acetonitrile (ACN) (≥99.9%), methanol (MeOH) (≥99.9%) and HPLC water were purchased from Merck. Formic acid, ammonium acetate and ammonium fluoride (≥96%, ACS reagent) were supplied by Sigma-Aldrich.

Fig. 1. Molecular structure of Congo red (A) and Methyl orange (B).

2.2. Apparatus

Experiments were performed in a pulsed light system XeMaticA-Basic-1L system (Steribeam, Kehl, Germany). The system has a 19-cm long xenon lamp placed at the top of the reactor and was worked at 2.5 kV.

The light pulse consists in flash with a duration of 200 μ s, an energy of 500 J that contained 21 % of UV light and a broad-spectrum emission which composition has been previously reported (Cudemos et al., 2013).

The dye sample was placed in a Petri dish without cover centred at 7.1 cm below the lamp. The Petri dish was positioned at top of a magnetic stirrer (Topolino, IKA, Staufen, Germany) that was used to homogenize the sample between pulses (fig. 2). The fluence incident on the sample was 2.14 J/cm^2 . Dosimetry was carried out by the analysis of in-built photodiode readings registered by a PC-Lab 2000 LT PC oscilloscope (Velleman Instruments, Gavere, Belgium) and PL system manufacturer performance charts. Fluence was increased by applying multiple pulses.

Fig. 2. Schematic representation of a pulsed light system. (For colour reproduction on the web and in black-and-white in print).

2.3. Experimental procedure

The experimental design was based in a reaction mixture of 20 ml volume containing Congo red or Methyl orange, mixed with hydrogen peroxide and water. Treatments were carried out up to 45 light pulses. Samples were withdrawn every five pulses and then samples were poured back into the reaction mixture in order to keep its volume and the distance lamp-sample surface constant.

Colour degradation was monitored by measuring the absorbance at specific wavelengths. Absorbance was measured at 465 nm for Methyl orange. Congo red decolouration was measured at 566 nm for pH 1.0, 540 nm for pH 3.5 and 498 nm for pH ≥ 6.0 since absorption spectra at different pHs did not show a clear isosbestic point (Fig. S1). The change in absorbance was linearly proportional to dye concentration within the measuring range. Tests were run at least per duplicate. Control tests were also performed replacing H₂O₂ for water (photolysis control), or without applying light pulses (H₂O₂ effect control). The H₂O₂ control was run for the same duration of the PL treatment.

Different tests were carried out changing the concentration of H₂O₂ or dye, or adjusting pH; one variable at a time while keeping the others constant. The concentrations of dye and H₂O₂ were selected for every dye independently according to preliminary tests in order to have initial absorbances high enough to enable monitoring colour changes. Typical concentrations were 15 mg/L (22 mM) for Congo red and 10 mg/L (31 mM) for Methyl orange; H₂O₂ concentrations were > 350 times higher than dye concentration on molar basis so that H₂O₂ concentration could be considered constant during the whole experiment. pH was adjusted by adding minimal amounts of concentrated NaOH or HCl. The effect of potential inhibitors was tested by addition of NaCl, Na₂SO₃ or Na₂CO₃ to a final concentration of 1 g/L. Generation of hydroxyl radicals was assessed by the incorporation of different amounts of ethanol, a well-known hydroxyl scavenger, to the reaction mixture.

The effect of the incorporation of the ferrioxalate complex to the dye/H₂O₂ mixture was also assayed. To this, different concentrations of sodium oxalate

1 and iron nitrate were combined (2.17-12.99 mg/L and 9.69-58.16 mg/L final
2 concentrations respectively) keeping a molar ratio iron:oxalate of 1:3.2 (Hislop
3 and Bolton, 1999). The pH was adjusted to 2, and the mixture was kept 30 min
4 in darkness before use in order to allow the generation of the ferrioxalate
5 complex. The ferrioxalate solution was added to a Methyl orange/H₂O₂ mixture
6 with final concentrations of 10 mg/L Methyl orange and 400 mg/L H₂O₂
7 respectively and treated with PL.
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10 2.4. Analytical methods

11 Spectrophotometric determinations were performed using a UV-vis
12 spectrophotometer (UV-1700, Shimadzu, Japan). pH was measured by a
13 Crison pH meter (Basic 20, CRISON, Barcelona, Spain). Temperature was
14 monitored by an infrared thermometer (ScanTemp 410, TFA Dostmann,
15 Wertheim, Germany).
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18 2.5. Detection of intermediaries

19 For detection of intermediaries, a 300 µL aliquot of a water-based colorant
20 solution, 600 µL of 5 mM ammonium acetate in water and 100 µL of MeOH
21 were transferred to a 2-mL vial for the analysis (90:10, v/v).
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23

24 2.5.1. Liquid chromatography separation

25 Liquid chromatography separation was performed using a SCIEX ExionLC™
26 AD system (Sciex, Redwood City, CA, U.S.) with a Hibar® HR Purospher®
27 STAR RP-C18 column (100 mm x 2.1 mm i.d., 2 µm particle size, Merck),
28 maintained at 40 °C in the column oven. Chromatography for high-throughput
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1 qualitative analysis employed a fast gradient with a 10 minute run time
2 composed of 2 mM ammonium fluoride in water (A) and ACN (B) for negative
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4 electrospray ionization and 5 mM ammonium acetate and 0.1% of formic acid in
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6 water (A) and ACN (B) for positive mode. The flow rate was of 0.5 mL/min, the
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8 injection volume was 10 μ L, and the auto-sampler temperature was maintained
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10 at 8 °C. A blank sample (MeOH) was injected after each sample to reduce
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12 carryover and to clean the column from any residue of colorant.
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17 2.5.2. MS and MS/MS conditions

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21 Qualitative TP samples were acquired using information dependent acquisition
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23 (IDA). Samples were analyzed using a SCIEX X500R QTOF system (Sciex,
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25 Redwood City, CA, USA) with Turbo V™ source and Electrospray Ionization
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27 (ESI) and operating in negative/positive polarity.
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33 The time-of-flight (TOF) acquisition covered m/z 100-1200. While high
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35 resolution product ions collected with IDA acquisition in both positive and
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37 negative ion mode occurred over the mass range m/z 50-1150. TOF and high
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39 resolution product ion extraction widths were 10 mg/L for positive and negative
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41 ion data. An inclusion list with the parent compounds and the most probable
42
43 candidate ions was included. The source conditions for the system were
44
45 optimized as follow. Ion Spray Voltage was set to 5500 V. Source temperature
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47 and nitrogen gas flows (Atomizing gas, GS1 and Auxiliary gas, GS2) were set to
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49 300° C and 50 psi, respectively. Curtain gas was set to 30 psi, Declustering
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51 Potential (DP) was set to 50 V (-50 V for negative). Collision Energy (CE) was
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53 set to 35V (-35V) with a collision energy spread of ± 15 V.
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Any drift in the mass accuracy of the SCIEX Q-TOF was automatically corrected and maintained throughout batch acquisition by infusion of Reserpine reference standard ($C_{33}H_{40}N_2O_9$, m/z 609.28066) for positive ionization, and a cluster of trifluoroacetic acid ($5(TFA-Na)+TFA^-$, m/z 792.85963) for negative mode. Calibration was running every 5 samples during the batch acquisition making use of the Calibrant Delivery System (CDS).

Qualitative data sets were processed with SCIEX OS 1.4.1 and MarkerView 1.3.1. (Sciex, Redwood City, CA, U.S.).

2.6. Kinetic data processing

Pseudo-first order constants were calculated by regressing absorbance vs. fluence plots according to Eq. (1):

$$\ln A/A_0 = -k F \quad (1)$$

where A is the absorbance at fluence F (J/cm^2), A_0 the initial absorbance and k the pseudo-first order rate constant (cm^2/J).

Data was processed by using Excel 2010 (Microsoft, USA).

3. Results and discussion

3.1. PL/H₂O₂ process

The efficacy of a PL technology to be used as part of an AOP was studied in this work. Each one of the factors, PL and H₂O₂, applied alone, was unable to

1 decolour the dyes significantly (fig. 3). Even though the dyes absorb in the UV
2 range (fig. 4) and PL lamp emits a significant portion of UV light (Cudemos et
3 al., 2013), the effect of direct photolysis was negligible. Direct photolytic effects
4 have been reported for other light sources but no attempt was made in this
5 research to reach similar decolourization levels because they required energy
6 and treatment times considered too long for the goals of the present work. As
7 examples, a direct photolytic effect on Congo red was observed by Murcia et al.
8 (2011) using a KrCl excilamp, but one hour of treatment was needed to reach
9 75 % decolourization. The direct photolysis using a low-pressure mercury lamp
10 has resulted less efficient, requiring two hours to reach 50 % decolouration of a
11 10 mg/L Congo red solution (Kamel et al., 2009).
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Fig. 3. Decolourization of Congo red (A) and Methyl orange (B) under a PL/H₂O₂ process. Congo red: [dye] = 15 mg/L, [H₂O₂] = 450 mg/L, pH = 6.0. Methyl orange: [dye] = 10 mg/L, [H₂O₂] = 400 mg/L, pH = 8.6. Bars represent standard deviation. (For colour reproduction on the web and in black-and-white in print).

Fig. 4. Evolution of the absorption spectrum of Congo red (A) and Methyl orange (B) with the progress of a PL/H₂O₂ process. Congo red: [dye] = 15 mg/L, [H₂O₂] = 450 mg/L, pH = 6.0. Methyl orange: [dye] = 10 mg/L, [H₂O₂] = 400 mg/L, pH = 8.6. (For colour reproduction on the web and in black-and-white in print).

When both factors, PL and H₂O₂, were combined to give place to a PL/H₂O₂ process, the decolourization markedly improved (fig. 3). This process can be consequently described as **following** a typical UV/H₂O₂ AOP, where light splits

H_2O_2 molecules in hydroxyl radicals that will later attach the dye, as represented in equations 3 and 4:

This suggestion is supported by tests carried out adding ethanol to the reaction mixture (fig. 5), where the degradation rate of the dyes was decreased by more than 35 %. This is consequence of the scavenger action of ethanol on hydroxyl radicals, which leaves less radicals to attack dye molecules (Mahmoodi et al., 2018).

Fig. 5. Inhibition of decolourization rate by the action of a hydroxyl scavenger. Congo red: [dye] = 15 mg/L, [H₂O₂] = 450 mg/L, pH = 6.0. **Methyl orange:** [dye] = 10 mg/L, [H₂O₂] = 400 mg/L, pH = 8.6. **Methyl orange (ferrioxalate):** [dye] = 10 mg/L, [H₂O₂] = 400 mg/L, pH = 2.0, [Fe(NO₃)₃ · 9H₂O] = 39 mg/L, [Na₂C₂O₄] = 8.7 mg/L. (For colour reproduction on the web and in black-and-white in print).

The PL/H₂O₂ process has typical characteristics of other UV/H₂O₂ processes, but could provide faster effects, yet, any comparison is rough because results depend on experimental set-ups, specially reactor configuration. It can be

1 observed (fig. 3) that more than 50 % decolouration of both dyes has been
2 achieved after applying 25 light pulses. Typical commercial PL systems can
3 work at pulse repetition rates of 3 Hz (Wang et al., 2016), therefore, they are
4 able to provide the energy required by this AOP in about 9 seconds. This
5 treatment is significantly faster than AOP driven by other light sources, which
6 can last several minutes or hours, even though.

14 The interval between light pulses is not expected to have a significant effect on
15 dye degradation. The generation of hydroxyls is a photochemical process, and
16 as such, it depends on fluence. Once generated, hydroxyl radicals are expected
17 to disappear during the interval between pulses because of their very fast
18 reaction rates. Rate constants of reaction with organic molecules are usually in
19 the order of 10^6 - 10^9 1/M s (Andreozzi et al., 1999).

27 The use of H₂O₂ was initially selected for this research as the simplest example
28 to test the effect of PL technology as part of an AOP, but it can be thought that
29 PL could yield even better results if combined with appropriated photocatalyst
30 selected among the wide variety of them currently existing (Ma et al., 2018;
31 Sacco et al., 2018; Sharma et al., 2018).

42 In spite of PL has been classified as a non-thermal method, it can warm up
43 samples as a collateral effect due to the infrared portion of its spectrum.
44 Consequently, temperature is usually monitored during its application (Gómez-
45 López et al., 2007). The increase in temperature in these tests has been < 3 °C;
46 which allows considering that they were run under isothermal conditions. It has
47 been demonstrated that this kind of reactions are not sensitive to small

temperature changes in the range 22-45 °C due to their low activation energy (Galindo and Kalt, 1998).

3.2. Changes in spectral characteristics during the decolourization process

Fig. 4 shows the absorption spectrum of the two dyes measured at the natural pH's of its respective reaction mixtures. Both spectra exhibit an absorption band in the visible range due $\pi \rightarrow \pi^*$ transitions in the azo bonds. The weaker absorption bands of Methyl orange to the $\pi \rightarrow \pi^*$ transitions located in the benzene rings. The bands fade with increasing fluence as consequence of the AOP. Hypsochromic shifts observed during degradation of Congo red and Methyl orange are associated with degradation products having spectral characteristics different from the parent molecule.

Dye decomposition was incomplete since there was still some absorbance at the end of the treatment under the assay conditions, especially in the UV region. For example, 12 % of the absorbance of Congo red still persisted at 96 J/cm², therefore, complete mineralization is not expected under the experimental conditions used in this research. This is not a peculiar weakness of the assayed process but a characteristic of azo dye degradation, which is related to the generation of recalcitrant by-products. The complete mineralization of Congo red is relatively difficult in comparison with that of other dyes. Lachheb et al. (2002) tested the mineralization of five dyes by using UV/TiO₂, Congo red was the only dye that was not fully mineralized after 180 min of treatment; while Thomas et al. (2016) achieved only 80 % mineralization after four hours using a nanocomposite hydrogel under direct sunlight irradiation. Full mineralization of Methyl orange is also difficult; only 67 %

reduction of the chemical oxygen demand of a MO solution was achieved by Jiang et al. (2012) using a non-thermal plasma AOP for 20 min of treatment, and Li et al. (2014) reported 80 % chemical oxygen demand abatement in a MO solution after three hours of treatment with sodium persulfate activated with zero-valent zinc.

3.3. Effect of H_2O_2 concentration

The rate of decolourization of the two dyes increase with the concentration of H_2O_2 (fig. 6, tables 1-2), which is a consequence of a bigger generation of hydroxyl radicals for attacking dye molecules. A higher availability of H_2O_2 increases the amount of hydroxyl radicals generated by the process, which accelerates degradation rates. However, this trend stops at relatively high H_2O_2 concentrations where a further increase in H_2O_2 concentration does not affect decolourization rates. This is result of hydroxyl self-quenching at high H_2O_2 concentrations as shown in equations 5 and 6 (Wang and Xu, 2012):

$HO_2\cdot$ radicals are less reactive than $\cdot OH$, therefore, its increasing concentration has a negligible contribution to dye degradation (Daneshvar et al., 2008) and can even decrease dye degradation at very high concentrations of H_2O_2 (Zuorro and Lavecchi, 2013).

Fig. 6. Effect of H_2O_2 concentration on the decolourization of Congo red (A) and Methyl orange (B) subjected to a PL/ H_2O_2 process. Congo red: [dye] = 15 mg/L, pH = 6.0. Methyl orange: [dye] = 10 mg/L, pH = 8.6. Bars represent standard deviation. (For colour reproduction on the web and in black-and-white in print).

Table 1. Pseudo-first rate constants for decolourization of Congo red by a pulsed light/H₂O₂ process under different dye and H₂O₂ concentrations and pHs with fluence up to 96 J/cm².

[H ₂ O ₂]	[Dye]	pH	k (cm ² /J)	R ²
100	15	6.0	0.0125	0.98
300	15	6.0	0.0194	0.98
450	15	6.0	0.0223	0.98
900	15	6.0	0.0233	0.97
1500	15	6.0	0.0262	0.98
2000	15	6.0	0.0256	0.98
450	2.5	6.0	0.0372	0.99
450	5.0	6.0	0.0295	0.99
450	15.0	6.0	0.0230	0.98
450	25.0	6.0	0.0222	0.99
450	30.0	6.0	0.0199	0.99
450	15	1.0	0.0026	1.00
450	15	3.5	0.0050	0.95
450	15	6.0	0.0220	0.99
450	15	9.0	0.0237	0.99
450	15	12.0	0.0230	1.00

Table 2. Pseudo-first rate constants for decolourization of Methyl orange by a pulsed light/H₂O₂ process under different dye and H₂O₂ concentrations and pHs with fluence up to 96 J/cm².

[H ₂ O ₂]	[Dye]	pH	k (cm ² /J)	R ²
100	10	8.57	0.0057	1.00
200	10	8.57	0.0178	1.00
300	10	8.57	0.0258	0.99
400	10	8.57	0.0419	0.98
500	10	8.57	0.0424	0.96
400	2.5	8.57	0.0508	0.99
400	5.0	8.57	0.0470	1.00
400	10.0	8.57	0.0419	0.98
400	15.0	8.57	0.0235	1.00
400	20.0	8.57	0.0191	0.98
400	10	2.03	0.0563	0.99
400	10	4.01	0.0427	0.99
400	10	5.99	0.0323	0.99
400	10	8.57	0.0419	0.98
400	10	10.0	0.0276	0.99

3.4. Effect of initial dye concentration

It is important from an application point of view to study the dependence of dye decolouration on the initial concentration of dye. The effect of the initial concentration of Congo red and Methyl orange on their decolourization rates was studied. Initial dye concentration plays a major role and significantly influence the degradation rate (fig. 7). The decolourization declined at increasing dye concentrations (tables 1-2), for example, the pseudo first reaction rate of Congo red gets reduced 47 % when initial dye concentration changes from 5 to 30 mg/L. This finding is caused by the attenuation of light through the dye solution, which increases with dye concentration. Therefore, lower amounts of hydroxyl radicals can be formed because less photons can reach H_2O_2 molecules. The presence of intermediate products may also play a role in the observed effect by consuming more hydroxyl radicals (Bali, 2004).

Fig. 7. Effect of dye concentration on the decolourization of Congo red (A) and Methyl orange (B) subjected to a PL/H₂O₂ process. Congo red: [H₂O₂] = 450 mg/L, pH = 6.0. Methyl orange: [H₂O₂] = 400 mg/L, pH = 8.6. **Bars represent standard deviation.** (For colour reproduction on the web and in black-and-white in print).

3.5. Effect of initial pH

The effect of the pH of the dye solution on decolourization of dyes depends on both, hydroxyl radical and dye properties. Generally, the decolourization of dyes by AOP is slower at high pH because under alkaline conditions H_2O_2 is converted to its less reactive conjugated base (Buxton et al., 1988). However, the results found in the current research show that the decolourization of Congo red is faster at high pH. In fact, the results can be clustered into two very distinct groups, a group of high decolourization rates at mildly acidic to alkaline conditions and another group of low decolourization rates at highly acidic conditions (fig. 8). This kind of results can be attributed to dye structure. At pH > 5.3, Congo red exists with an azo structure. When the pH is decreased the dye protonates giving place to forms with at least two tautomeric quinoid structures, an ammonium and an azonium form (where one proton is added to the α -azo nitrogen). These structures render a stable chelate ring with the azo group and the amino group and the oscillation of a proton between them (Pigorsch et al., 1994).

It has also been postulated that dyes containing two sulfonic groups, such as Congo red, can produce aggregates of several molecules that are less accessible to hydroxyl radicals than single molecules (Galindo et al., 2001). Actually, the aggregation of Congo red molecules upon acidification was observed in the fundamental studies by Pigorsch et al. (1994).

From the point of view of hydroxyl radical stability to pH, given that HCl was used to decrease pH, it is possible that the chloride ion reacts with hydroxyl radicals according to eq. 7 (Jayson et al., 1973) leading to inorganic radical ion,

which shows lower reactivity than hydroxyl radicals, so that they do not take part in the dye decolourization (Aleboye et al., 2005).

Fig. 8. Effect of initial pH on the decolourization of Congo red (A) and Methyl orange (B) subjected to a PL/ H_2O_2 process. Congo red: $[\text{dye}] = 15 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 450 \text{ mg/L}$. Methyl orange: $[\text{dye}] = 10 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$. Bars represent standard deviation. (For colour reproduction on the web and in black-and-white in print).

On the other hand, the decolourization of Methyl orange is higher at low pH. This effect has been attributed to protonation of the dye at low pHs, where a labile hydrogen atom makes the dye more vulnerable toward attack of hydroxyl radicals (Galindo & Kalt, 1998).

3.6. Effect of salts

Various salts are added in the bath of textile industries as auxiliaries of the dying process, which can act as radical scavengers. The radical scavenging activity of inorganic salts is generally attributed to the generation of new radicals with lower reactivity than $\text{OH}\cdot$, even though some cases have been reported where certain anions can enhance degradation efficiency (Aleboyeh et al., 2012). Therefore, the effect of NaCl , Na_2SO_3 and Na_2CO_3 on decolourization of Congo red and Methyl Orange by the $\text{PL}/\text{H}_2\text{O}_2$ process was tested (fig. 9). In general, the inhibitory effect was stronger for SO_3^{2-} and weaker for NaCl . SO_3^{2-} was also the strongest inhibitor of Congo red decolourization among eight salts tested by Sun et al. (2009). It is known that sulphite reacts with hydroxyl radicals with very high constant rates, near the diffusion-controlled limit (Neta and Huie, 1985).

Fig. 9. Effect of different salts on the decolourization of Congo red (A) and Methyl orange (B) subjected to a PL/H₂O₂ process. Congo red: [dye] = 15 mg/L, [H₂O₂] = 450 mg/L, pH = 6.0. Methyl orange: [dye] = 10 mg/L, [H₂O₂] = 400 mg/L, pH = 8.6. **Bars represent standard deviation.** (For colour reproduction on the web and in black-and-white in print).

NaCl inhibits dye degradation because Cl⁻ reacts with OH[•] according to Eq. 7 and carbonate acts as a radical scavenger by producing the much less reactive CO₃^{•-} according to the Eq. 8 (Andreozzi et al., 1999).

The inhibitory effect of these salts occurs as long as hydroxyl radicals exist in dye solution. It starts during the pulse, when hydroxyl radicals are generated, and will persist until these are depleted. The depletion should occur very fast given the high constant rates of the reaction between hydroxyls and salts, which are 5.5×10^9 , 4.3×10^9 and 3.9×10^8 1/M s for SO_3^{2-} (Neta and Huie, 1985), Cl^- (Jayson et al., 1973) and CO_3^{2-} (Buxton et al., 1988) respectively.

In order to overcome the inhibitory effects of inorganic salts in a real-life scenario, several strategies are possible, the separation of those salts from the effluent before proceeding with AOP process, or the use of higher fluences.

3.7. Generation of degradation products

The generation of degradation products during the PL/ H_2O_2 -based dye treatment was monitored by LC-HRMS which allowed to detected and tentatively identify several compounds. The three degradation products observed for Congo red are listed in Table 3. The TP403 at m/z 402 corresponds to the loss of the azonaphthalene moiety. TP 666, in turn, is proposed to be formed from Congo red by oxidative conversion of one of the amino group to the nitroso derivative. The third product, the TP650 with an m/z of 324 is attributed to dehydrogenation upon formation of an extended conjugated system. It worth noting that no benzidine, a known carcinogen (IARC, 2012), was detectable during the catalytic breakdown of Congo red. Additionally, the conservation of the azo group at this stage of the oxidation as it has been reported to occur for Congo red degraded by other AOPs such as

TiO₂ photocatalysis (Erdemoğlu et al., 2008) and a photo Fenton like process (Devi et al., 2009).

Table 3. Transformation products (TP) identified during the degradation of Congo red by a PL/H₂O₂ process.

m/z of [M-H] ⁻	Structure	TP name
324.0448		TP650
402.0918		TP403
664.0846		TP666

A larger number of degradation products was observed in the experiments with Methyl orange (Table 4). The parent compound gave rise to a desulfonated and N-demethylated compound (TP255), three hydroxylated and demethylated compounds (TP293, TP307 and TP323), two demethylated compounds (TP277 and TP291), an hydroxylated compound (TP 321) and an hydroxylated compound with cleavage of the bond between the azo group and one benzene ring. Compounds corresponding to TPs 277, 291, 321 and 323 have also been reported for the TiO₂ photocatalytic degradation of Methyl orange (Baiocchi et al., 2002).

Table 4. Transformation products (TP) identified during the degradation of Methyl orange by a PL/H₂O₂ process.

m/z of [M-H] ⁻	Structure	TP name
172.9914		TP173
254.0935		TP255
276.0448		TP277

290.0605

TP291

292.0398

TP293

306.0554

TP307

320.0711

TP321

322.0503

TP323

3.8. Effect of ferrioxalate complex on Methyl orange decolourization

The effect of PL as a light source in the frame of an AOP was firstly studied in a very basic system, an UV/H₂O₂ process. It can be thought that using system that is a bit more advanced could yield better results. Therefore, the incorporation of ferrioxalate to the PL/H₂O₂ was studied. The ferrioxalate complex was added to the combination of variables that produced the best

results for Methyl orange degradation, that is, 400 mg/L H_2O_2 at pH 2. This has the advantage that the ferrioxalate complex works better at acidic pH (Jeong and Yoon, 2005).

It can be observed in table 5 that the addition of ferrioxalate complex to the PL/ H_2O_2 system accelerated the decolouration rate of MO. Increasing ferrioxalate concentration accelerates the decolourization up to certain concentration beyond which the decolourization rate starts to decline, likely due to excessive hydroxyl generation. The results demonstrate that the PL/ H_2O_2 /ferrioxalate process is able to increase almost 3-fold the decolourization rate of MO. This conclusion is derived from the comparison of the rate constant of the treatment using 38.8 mg/L Fe^{3+} and 8.7 mg/L $\text{C}_2\text{O}_4^{2-}$ (0.1477 cm^2/J) with that of the treatment with no ferrioxalate (0.0523 cm^2/J). Less than 5 % of colour remained after applying just 21 J/cm^2 (10 light pulses) when using 38.8 mg/L Fe^{3+} , 8.7 mg/L $\text{C}_2\text{O}_4^{2-}$ and 400 mg/L H_2O_2 for 10 mg/L of dye.

Table 5. Pseudo-first rate constants for decolourization of Methyl orange by a pulsed light/ H_2O_2 process under different ferrioxalate concentrations with fluence up to 96 J/cm^2 . [dye] = 10 mg/L, [H_2O_2] = 400 mg/L, pH = 2.0.

[Fe^{3+}] (mg/L)	[$\text{C}_2\text{O}_4^{2-}$] (mg/L)	k (cm^2/J)	R^2
0	0	0.0523	1.00
9.7	2.2	0.0689	0.99
19.4	4.3	0.0996	1.00
29.1	6.5	0.1112	1.00
38.8	8.7	0.1477	0.99
48.5	10.8	0.0877	1.00

Even though a direct comparison between our results and those that can be found in the literature reporting on different dye degradation methods should not be done because of differences in experimental approaches, a gross comparison can reveal the main advantage of including PL in an AOP for dye degradation. The time needed to achieve 95 % decolouration of MO solutions is 19 min as the best (Devi *et al.* 2009; Wang and Bai 2016; Lee *et al.* 2016; Chen *et al.* 2017; Ljubas *et al.* 2015). In comparison, 21 J/cm² is required to attain the same effect on a MO solution when using the PL/H₂O₂/ferrioxalate process, that level of energy can be supplied by PL commercial systems in four seconds. The comparison supports our statement that PL can provide very fast dye degradation, which would allow the implementation of fast/compact wastewater treatment reactors that would yield cleaner dying industries.

4. Conclusions

Fast decolourization of two azo dyes by a PL AOP was demonstrated in this research. The decolourization follows the pseudo-first order kinetic with high rates at low dye concentration or increasing H₂O₂ concentrations up to a maximum. The efficacy of the process is affected by pH in a different way depending on the dye. SO₃²⁻, Cl⁻ and CO₃²⁻ ions inhibit dye decolourization. No known toxic intermediaries were identified. The incorporation of the ferrioxalate complex to form a pulsed light/H₂O₂/ferrioxalate process increase more than twice the decolourization rate of Methyl orange. This result also shows, beyond

the enhanced efficacy of the system, that pulsed light integrated as light source in AOP systems other than a simple pulsed light/H₂O₂ process can accelerate dye degradation. It is hypothesized that the use of PL coupled to state-of-the-art photocatalyzers may yield even better results. PL technology could become an alternative light source to contribute to decrease the environmental impact of wastewater produced by the dyeing industry.

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Highlights

- An advanced oxidation process using pulsed light technology was tested.
- A pulsed light/H₂O₂ process can decolourize different azo dyes.
- The decolourization provided by a pulsed light/H₂O₂ process is very fast.
- Ferrioxalate complex enhances the efficacy of the pulsed light/H₂O₂ process.

Figure S1. Effect of pH on the absorption spectrum of Congo red.

Dear Prof. Kleměš

We are sending hereby a request to include a new co-author in fulfillment with the following requirements of the journal:

Any addition, deletion or rearrangement of author names in the authorship list should be made only **before** the manuscript has been accepted and only if approved by the journal Editor. To request such a change, the Editor must receive the following from the **corresponding author**: (a) the reason for the change in author list and (b) written confirmation (e-mail, letter) from all authors that they agree with the addition, removal or rearrangement.

We request the addition of Dr. Sandra Pérez Solsona, from the Water and Soil Quality Research Group, Department of Environmental Chemistry, IDAEA-CSIC, Jordi, Girona, Barcelona, Spain.

The specific points are as follow:

(a) The reason for the change in author list.

We sub-contracted this laboratory in order to study the intermediaries produced during the degradation of the dyes. However, we believe that the effort made by Dr. Pérez has gone beyond what we have sub-contracted. More importantly, the scientific input made by Dr. Pérez in the discussion of our work has led us to think that she has become indeed a co-author and must appear in the list of co-authors as such.

(b) Written confirmation (e-mail, letter) from all authors that they agree with the addition.

Below we include the signatures of the original co-authors accepting the addition.

Sofía Martínez-López

Ana Serrano-Martínez

Carmen Lucas-Abellán

María Teresa Mercader-Ros

Nerea Cuartero

Patricia Navarro

José Antonio Gabaldón

Vicente M. Gómez-López

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Dear Prof. Kleměš

In fulfillment with the following requirement of the journal:

In the case of addition or removal of authors, this includes confirmation from the author being added or removed.

I confirm that I wish to be included as new co-author of the manuscript titled:

Pulsed light for a cleaner dyeing industry: azo dye degradation by an advanced oxidation process driven by pulsed light,

coded JCLEPRO-S-18-01047

Yours sincerely

Dr. Sandra Pérez Solsona

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